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学位論文題目 Novel Catalytic Activity of Gold Nanoclusters

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In this thesis, the novel catalytic activities of gold nanocluster were investigated using gold nanocluster stabilized by hydrophilic polymer, poly(*N*-vinyl-2-pyrrolidone) (Au:PVP). It was a common sense that metallic gold does not possess any catalytic activity due to its unreactive character. Since the first report by Haruta in 1987 that the nano-sized gold cluster supported on metal oxide did catalyze the CO oxidation, lots of studies about the characteristic features of nanocluster as an aerobic oxidation catalyst. However, the gold nanocluster should have comprehensive catalytic activities. Therefore, the investigation of catalytic activity of gold nanocluster is important to understand the character of gold nanocluster.

This thesis consists of 6 Chapters. In Chapter 1, general introduction is described. Gold nanoclusters (average size: 1.3 nm) stabilized by hydrophilic polymer, poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) behave as *quasi*-homogeneous catalyst. The small size of Au:PVP, which has narrow size distribution, was prepared by reducing H₂AuCl₄ with NaBH₄ under a low-temperature aqueous solution of PVP. It has been reported that Au:PVP act as not only oxidation catalyst but also formal Lewis acid which exhibits a high catalytic activity toward oxidation of alcohols, homocoupling reaction/hydroxylation of organoboron compounds in aqueous solvent and intramolecular hydroalkoxylation. In every case, it was proposed that superoxo-like species generates on the cluster surface under *quasi*-homogeneous conditions would play a key role as an active species.

In Chapter 2, intramolecular hydroamination of toluenesulfonamides to unactivated alkenes is described. Intramolecular hydroamination of amides have been extensively studied promoted by transition metal complex, alkali metal, and so on. However, the reactivity of the catalysts is highly dependent on the substituent on nitrogen and electron density on alkene, no versatile catalyst for the various types of amine derivatives is known. On the other hand, Au:PVP behaves as formal Lewis acid catalyst, which catalyze the intramolecular hydroalkoxylation in protic solvent under basic and aerobic conditions. As a similar type of reaction with intramolecular hydroalkoxylation, intramolecular hydroamination, intramolecular hydroamination of toluenesulfonamides was investigated. The intramolecular hydroamination of toluenesulfonamides proceeded quantitatively in EtOH in presence of Cs₂CO₃ as a base under basic and aerobic conditions. The labeled experiment revealed that EtOH is hydrogen source of products. Au:PVP has high catalytic activity for intramolecular hydroamination of toluenesulfonamides in protic solvent under basic and aerobic conditions.

In Chapter 3, intramolecular hydroamination of primary amines to unactivated alkenes is described. Intramolecular hydroamination of primary amines have been studied extensively using lanthanide complex and group IV complex. However it is usually sensitive for moisture and oxygen. On the other hand, Au:PVP is stable to moisture-/oxygen-stable catalyst, which has high catalytic activity for intramolecular hydroamination of toluenesulfonamides, Therefore, it is expected that Au:PVP can be versatile catalyst, which worked as a moisture-/oxygen-stable catalyst for the hydroamination of primary amines. While the reaction of primary amine did not proceed under basic conditions, the reaction underwent effectively in presence of formate as an additive in protic solvent under neutral to slightly acidic conditions. From the result of labeling experiment, it is found that the hydrogen at the methyl group of product is introduced from formyl group of formate, which may indicate that EtOH cannot adsorb effectively onto gold surface due to the neutral to slightly acidic condition. Au:PVP has high catalytic activity for not only toluenesulfonamide, but also intramolecular hydroamination of primary amines in protic solvent under neutral to slightly acidic conditions.

In Chapter 4, the reaction of *N*-benzyl alkenylamines is described. The catalytic activity of Au:PVP for intramolecular hydroamination of secondary alkylamines to unactivated alkenes was investigated. The

intramolecular hydroamination proceed in presence of Cs_2CO_3 in EtOH, giving corresponding *N*-benzyl pyrrolidines in moderate yield. In addition unexpectedly, *N*-benzyl pyrrolidinone was also obtained as a minor product, suggesting that ozonolysis-type oxidative carbon-carbon bond cleavage would occur. There was no report of ozonolysis-type oxidation under aerobic conditions. The yield of the pyrrolidinone was increased by changing a base to CsOAc. When *N*-benzyl alkynylamine was used as a substrate, *N*-benzyl pyrrolidinone was obtained predominantly. The result indicated that *N*-benzyl pyrrolidinone may be corresponding *N*-benzyl-*exo*-methylene pyrrolidine or its derivatives might be an intermediate for the formal-ozonolysis product.

In Chapter 5, aerobic oxygenation for benzyl ketone is described. It has been reported Au:PVP exhibits a high catalytic activity toward aerobic oxidation reaction such as oxidation of alcohols, homocoupling reaction/hydroxylation of organoboron compounds in aqueous solvent. However no oxygen atoms are introduced into the products in the above reaction, except in the case of hydroxylation of organoboron compounds. Oxygenation reaction was extensively studied using metal oxide-supported gold nanocluster, which was used as heterogeneous catalyst, however homogeneous oxygenation reaction is hardly reported. From the result of hydroxylation of organoboron compounds, it is expected that Au:PVP has high potential in oxygenation reaction in *quasi*-homogeneous catalyst system. Auto-oxidation reaction of benzyl ketone with cleavage the carbon-carbon bond, giving the corresponding ketone and carboxylic acid, is usually carried out in polar aprotic solvents under strong basic conditions such as *t*-BuOK/DMSO, which does not proceed in protic solvents, in protic solvents, particularly water, under weakly basic conditions. Au:PVP promote the auto-oxidation-type reaction and α -hydroxylation reaction of benzylic ketones by changing the base and solvent conditions. From the reaction monitoring by $^1\text{H-NMR}$ reveals that Au:PVP accelerate the formation of α -peroxide. Au:PVP promote the auto-oxidation-type reaction and α -hydroxylation reaction of benzylic ketones, which selectivity is controlled by changing the solvent and base conditions.

In conclusion, Au:PVP catalyst can be versatile and easy-to-handle π -Lewis acid catalyst as well as aerobic oxidation catalyst. In addition, it is expected that unforeseen new type of reaction is developed such as cleavage of carbon-carbon bond in the reaction of *N*-benzyl alkylamines using Au nanocluster catalyst.

この学位論文は金ナノクラスター触媒を用いた新規合成反応の開発に関して記述され、序論（第1章）と結論（第6章）を含めて全6章で構成されている。

第2章では、スルホンアミドのアルケンへの分子内付加反応に関して述べている。炭素-炭素多重結合に対するアミン類の分子内付加反応は、含窒素複素環合成において重要な反応である。本反応の進行には触媒が必要であるが、従来知られている触媒の多くは水や酸素に対して不安定であり、特殊な条件での反応操作が必要であった。北原氏は、含水溶液中空気雰囲気下、形式的なルイス酸活性を示すという、金ナノクラスターの独特な触媒活性に着目し、水溶性ポリマーであるポリビニルピロリドン（PVP）で保護した金ナノクラスター（Au:PVP）を触媒として用いた、スルホンアミドのアルケンへの分子内付加反応の開発研究を行った。その結果、エタノールを溶媒かつ犠牲還元剤として用い、炭酸セシウムを塩基として用いることで、極めて効率的な環化付加反応の開発に成功している。また一部の水素を重水素で置換した反応基質を用いた実験により、本反応が金触媒によるアルケンの活性化を経て、アミドがアンチ付加する機構で進行していることを明らかにしている。

第3章では、前章の反応を1級アミンの反応へ展開した結果について述べている。アミンの付加反応において、アミンの保護基を用いず、すなわち1級アミンを直接反応基質に用いることができれば、原子効率の上でも極めて重要かつ有用である。しかしながら1級アミンはスルホンアミドとは全く異なる性質を有するため、これまでに知られている触媒は、ランタノイドや第4族遷移金属錯体触媒など、極めて酸素や水に鋭敏なものに限定されていた。今回、犠牲還元剤と溶液の酸性度を適宜選択することで、スルホンアミドの反応で用いたAu:PVP触媒を1級アミンの反応にも適用することができる事を見出した。このことは、金クラスター触媒が、反応条件を適宜選択する事により、極めて汎用的かつ水/酸素に安定な実用的な触媒となり得ることを示している。

第4章では、同様の手法を用いたベンジル保護アミンの反応について述べている。その結果、Au:PVP触媒存在下、炭酸セシウムを塩基として用いた場合、前章までの反応と同様な分子内付加が主反応として進行するのに対し、酢酸セシウムを塩基として用いた場合、形式的に環化の後さらに酸素化が進行した生成物に相当するラクタム化合物が得られるという、新しい反応が進行することを見出している。この新たな酸素化反応の反応機構として、ベンジルアミンの分子内付加の後、 α -水素脱離/ β -水素脱離を経て、ビニル金中間体が生成している事を示唆する結果を得ており、金ナノクラスターの触媒機能発現の機構解明につながる重要な結果であると言える。

第5章では、金クラスター触媒を用いたベンジルケトンの酸素化反応について述べている。反応条件を変えることで、自動酸化型炭素-炭素結合切断反応と α -ヒドロキシ化反応を選択的に進行させることができることを見出している。この場合、金クラスター触媒はベンジルケトンの α 位のペルオキシ化の過程を効率よく触媒していることを明らかにしている。

以上の結果はいずれも、これまで知られていなかった金ナノクラスター触媒の触媒活性を明らかにしており、当該分野の研究の発展に大きく貢献する内容である。これらの成果

のうち、第2章、第3章、および第5章の結果は既に国際誌に掲載され、高い評価を受けている。よって、本論文は博士（理学）の学位論文に値するものと認められる。